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Treatment Optimization of Electrocoagulation (EC) in Purifying Palm Oil Mill Effluents (POMEs)

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Abstract. Palm oil mill effluents (POMEs) can contaminate soil, groundwater, and also the water environment. The increasing production of crude palm oil in Indonesia produces an enormous amount of POME waste. Therefore, a method is needed that can be used to purify POMEs. In this paper, an electrocoagulation (EC) method for purification of wastewater and a design to optimize this method are presented. An optimization experiment was performed by varying voltage and process time. The applied voltages were 6, 9, and 12 V and the process time was varied between 30 and 150 minutes. The measured parameters were: COD, BOD₅, pH, TSS, lipids, and NH₃-N. The result shows that optimum conditions were achieved at a voltage of 12 V and a process time of 150 minutes with COD at 8000 mg/L, BOD₅ at 12000 mg/L, pH at 7.46, TSS at 324 mg/L, lipids at 17.8 mg/L, and NH₃-N at 0.65 mg/L. The results are in accordance with environmental quality standards for pure water. This study proves that the proposed EC method is effective in purifying POMEs from pollutants.

Keywords: *aluminum electrode; electrocoagulation (EC) optimization; POMEs; purifying; wastewater treatment.*

1 Introduction

Palm oil mill effluents (POMEs) that are disposed in the environment without any treatment can be dangerous, especially to water bodies such as rivers, swamps and lakes. POME production in Indonesia is estimated around 28.7 million ton each year. They are potential environmental pollutants due to their smell, COD and BOD contamination, and high total suspended solids. In most cases, POMEs consists of floating, dissolved solids and oil in water emulsions. Besides that, they usually also contain inorganic and organic compounds, some of which cannot be decomposed by microorganisms. In general, waste that contains organic compounds can be decomposed by bacteria using biological methods, i.e. biological wastewater treatment. This treatment can be applied to POMEs using aerobic and anaerobic processes [1,2]. Besides biological methods there are various other methods that can be applied to treat POMEs, i.e.

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hybrid anaerobic bioreactors [3,4], coagulation and flocculation using a coagulant [5-7], methane emission from anaerobic ponds [8], synthetic polyelectrolytes [9,10] and electrocoagulation (EC) [11].

Electrocoagulation (EC) is one of the most effective methods in wastewater treatment. It is popular since it can process the effluent into water that can be reused. The issue that arises nowadays is how to process industrial and domestic wastewater into pure water before disposing it to water inland. This has led to an increase in the number of researches looking for new and effective methods for purifying wastewater. Although several researches have already discussed the effectiveness of EC, there is always a desire to improve this technique in order to increase its effectiveness [12].

EC is based on an electrolytic cell that consists of a device that can make direct current (DC) electrical energy to produce an electrolysis reaction. The basic principle of EC is reduction and oxidation (redox). In addition to the electrode and EC reactions, the water that serves as electrolyte solution is also involved [13].

POMEs can be treated effectively using EC due to it is economy and environmental friendliness, and because the result from wastewaters processed by EC can fulfill the environmental quality standards for pure water. EC is a process of coagulation using a direct current that achieves electrolyte decomposition through electrochemical processes. The aim of this study was to determine the effects of voltage on the performance of the EC method and determine the best process time in POME treatment.

2 Materials and Methods

The EC method conducted in this study used aluminum for the anode and cathode. The EC process was done in batches. This was aimed at decreasing the concentrations of COD, BOD₅, TSS, lipids, and NH₃-N, and increasing the acidity of the POMEs, so that they will not pollute the environment when they are disposed in the environment.

1. POME samples

The POME samples came from several industries located in South Sumatra, Indonesia. The compositions of the POME samples in this study were characterized in order to assess the COD, BOD₅, TSS, NH₃-N, and lipid content.

2. Experimental setup

The experiment was conducted in batches as shown in Figure 1. The electrochemical unit consisted of an EC cell, a DC power supply and an aluminum electrode. In the experiments, two monopolar electrodes with the same dimensions acted as anode and cathode. These electrodes were separated from each other by a distance of 10 mm. The composition was kept the same by turning the speed of the stirrer up to 100 rpm. This speed was also intended to avoid the association of flocs in the solution. After one batch was completed, all of the electrodes were cleaned using HCl dilution. The whole experiment was conducted at room temperature [14].

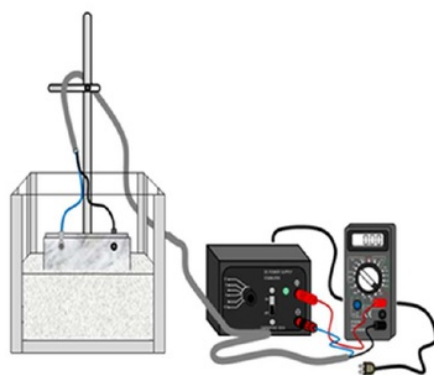


Figure 1 Scheme of the experimental unit.

3. Experimental procedure

The experiments in this study were conducted in batches using a 500-mL POME sample for each test. The samples were treated by EC cells with two electrodes as mentioned before. The voltage settings were 6, 9, and 12 V. The process time was set to 30, 60, 90, 120, and 150 minutes. The voltage was set up to 12 V because significant results can be achieved at this voltage. After each EC process, the samples were conditioned at room temperature for 15 minutes to let the flocs settle. The next treatment was collecting the supernatant sample to perform the determination of COD, BOD₅, pH, TSS, NH₃-N, and lipids.

4. COD, BOD₅ and TSS determination

The COD and BOD₅ of the POME samples before and after EC were determined based on standard methods for water and wastewater examination [15]. COD was analyzed using the closed reflux titrimetric method. This method involves refluxing the known volume of the samples with an oxidizing agent in a closed ampule at 150 °C for two hours and titrating the excess oxidizing agent with standard ferrous ammonium sulphate using ferroin as indicator. BOD₅ determination involves overflowing the sample into a BOD bottle of a specified size and incubating it at 20 °C temperature for 5 days. TSS determination was done using the gravimetric method.

5. Lipid determination

Lipid content was determined using extraction, i.e. by separating layers of water with a solvent. 10 gram Na₂SO₄ anhydrate filter was used to clean the solvent. The extraction was centrifuged for 5 minutes at an angular velocity of 2400 rpm. This method was conducted several times until no more emulsion was detected.

3 Results and Discussion

A comparison between the unprocessed POMEs and the POMEs processed using EC is shown in Table 1.

Table 1 Unprocessed and Processed POMEs

Properties/test	Unprocessed	Processed
BOD ₅ mgL ⁻¹	23700	12000
COD mgL ⁻¹	45000	8000
TSS mgL ⁻¹	12000	324
Lipids mgL ⁻¹	100.4	17.8
NH ₃ -N mgL ⁻¹	3.73	0.65
pH	4.48	7.46

3.1 ¹Effect of Voltage on Process time for COD

The COD is the quantity of oxidant that reacts with the samples in a certain condition. The amount of oxidant used is proportional to the oxygen need. Both organic and inorganic compounds in the sample are oxidized subjects, however, the organic compounds are more dominant. COD is often used as a measurement of the quantity of pollutants in water.

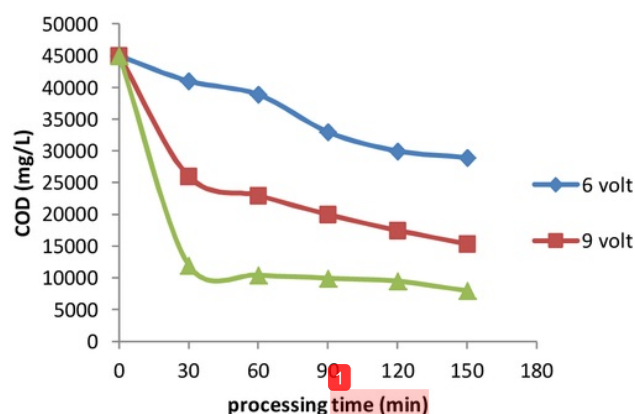


Figure 2 Effect of voltage on process time of COD.

Figure 2 shows that the best result in decreasing the COD of the POMEs after being processed using EC with 12 V was reached at 150 minutes. The COD in this condition decreased drastically, from 45000 mg/L to 8000 mg/L. From Figure 2, it can be concluded that the longer the contact time and the greater the voltage, the greater the reduction of COD. This is due to the reduction and oxidation processes in the EC reactor being faster along with the increase in voltage. At the electrodes, oxygen and hydrogen are formed; they affect the reduction of COD. The hydrogen gas brings colloid impurities to the surface of the reactor (flotation). This is characterized by the existence of a large quantity of bubbles or foam that brings the dirt to the surface of the reactor. Based on the double layer theory, the reduction of COD is due to the flocs formed by the organic ion compound associated with positive coagulant ions. The molecules in the effluent are turned into flocs, colloidal particles in the effluent that bind the particles [15].

The reduction of COD during EC occurs due to destabilization. Colloidal destabilization occurs by metal cations that form polyvalent polyhydroxide. This complex compound has high adsorption. Thus, it can simplify the process of aggregation with various pollutants to form large flocs that can be easily separated using a flotation technique through which the density of the material becomes smaller.

3.2 Effect of Voltage on Process time for BOD₅

Figure 3 shows the decreasing value of BOD₅ after the EC process. From the graph in Figure 3 it can also be seen that the best result of BOD₅ reduction was at a time of 150 minutes with a voltage of 12 V, where the BOD₅ value changed from 23700 mg/L to 3910 mg/L. Based on the graph in Figure 3, it can be concluded that the greater the voltage, the lower the value of BOD₅. This happens because the stability of the colloidal system suspended in the liquid waste samples is disturbed by the addition of aluminum ions coming from the oxidation process at the anode. Al³⁺ ions included in the samples reduce the zeta potential. This means that the charge difference on the surface of the samples is reduced. The reduction of this charge difference reduces the thickness of the diffuse layer and disturbs the stern layer. This reduces or eliminates the repulsive force between adjacent particles, which leads to coagulation. Compared to 6 and 9 V, drastic BOD₅ reduction occurred at 12 V. This is due to the voltage increase that is proportional to the current increase. This leads to a greater speed of the coagulated particles, which decreases the amount of suspended particles. The smaller the number of particles and the smaller the particles sizes, the bigger the currents needed and the longer the coagulation time.

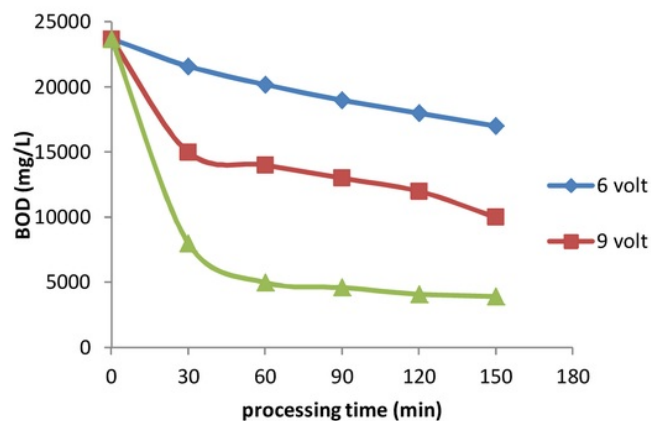


Figure 3 Effect of voltage on process time for BOD₅.

With the results of the BOD₅ analysis the quality of a water body can be determined. The quality of a water body is indicated by the amount of oxygen needed by microorganisms for decomposing the organic matter that occurs in

the water in aerobic state. A high BOD₅ plays an important role in determining the ability of the water body in supporting better growth of algae and aquatic organisms. The higher the number of the bacterial population, the higher the level of water pollution.

3.3 Effect of Voltage on Process Time for pH

Figure 4 shows that there was an increase in the pH of the POME samples from their initial pH 4.48 (acidic). After EC processing, the increase rate reached 7.46 pH (neutral). This condition had a pH range between 6 and 9 at 12 V and 150 minutes of process time. In the EC process, water electrolysis generates hydrogen gas and hydroxide ions. The longer the contact time, the faster the formation of hydrogen gas and hydroxide ions. The reduction reaction of water produces hydroxide ions with a coefficient greater than the coefficient of hydrogen. It is the same with the voltage, which also increases along with the increase of the current. The current is the flow of electrons. If the current is larger, the number of electrons flowing in the EC reactor also increases. The increasing number of electrons causes the number of OH⁻ and H₂ gas bubbles to increase as well. This indicates that more formation of hydroxide ions occurs when the voltage is higher and the process time is longer. This situation increases the acidity to close to or at neutral pH.

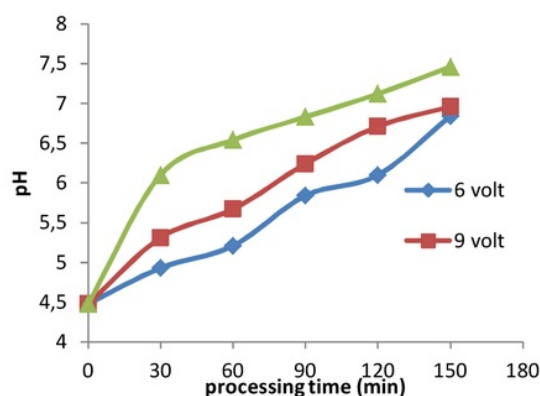


Figure 4 Effect of voltage on process time for pH.

The pH level is the concentration of hydrogen ions (H⁺) in the water. pH is very important as a water quality parameter because it can control the type and rate of the reaction of some materials in the water. The increase of the pH in the EC process is due to the alkalization of Al³⁺ ions that are added to the water. When

the addition happens, the water hydrolysis process causes a reaction with hydroxyl ions. This reaction produces $\text{Al}(\text{OH})_3$ and hydrogen ions.

3.4 Effect of Voltage on Process Time for TSS

Figure 5 shows the result of the treatment on the POMEs with EC. The best TSS reduction was achieved with a process time of 150 minutes at 12 V. The value dropped from its initial value of 12000 mg/L to 324 mg/L. The allowable maximum TSS level gained was 250 mg/L. The voltage is proportional to the current, i.e. if the voltage increases, the current flow also increases. Because the current is a flow of electrons, when the current is greater, the number of electrons flowing in the EC reactor also increases. The increasing number of electrons increases the number of OH^- and H_2 gas bubbles. OH^- gathers with Al^{3+} (anode) and forms complex compounds that bind the pollutants, forming flocs. The more OH^- is formed, the more flocs are produced. The increase of H_2 gas bubbles produced makes the flocs float to the surface more easily. Flocs that are formed, by and by grow larger and eventually settle on the bottom of the EC reactor [16].

The reduction of TSS had a great impact. This is because TSS are pollutants that have the form of a suspension. When the effluent contains a high TSS concentration, the effluent has poor quality. Thus, it has potential in damaging ecosystems, especially aquatic ecosystems. The sources of TSS are both organic and inorganic chemicals that form a suspension in the effluent. Besides that, the sources of TSS also come from metals that form complex compounds either with hydroxide anions or other compounds that are suspended in the effluent due to their molecular size or their polarity properties.

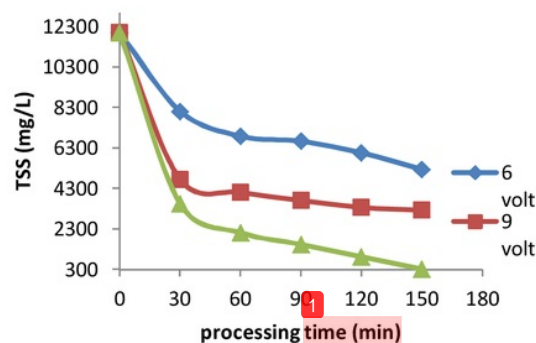


Figure 5 Effect of voltage on process time for TSS.

3.5 ¹ Effect of Voltage on Process Time for Lipids

Figure 6 shows the greatest decrease of oil/lipid value in the effluent after EC was applied. With a runtime of 150 minutes at 12 V it decreased from its initial value of 100.4 mg/L to 17.8 mg/L. In general, the quality standard for lipids is 25 mg/L. With 150 minutes process time at 12 V, the largest energy was produced, marked by an increase of the temperature in the waste and producing heat. This high temperature causes the kinetic energy of the atoms to increase. This is because more unstructured molecules in the waste increase the entropy and hence the possibility of collision is higher. This speeds up the hydrolysis reaction. The occurrence of the hydrolysis reaction causes damage to the oil or grease and it also produces fatty acids and glycerol. The presence of fatty acids and glycerol leads to unstability of the oil. Oil is a non-polar compound, while fatty acids and glycerol are polar compounds. Therefore, when the content of fatty acids and glycerol increases, the oil deteriorates more easily. The damage of oil/lipids decreases the value of the lipids since the compound has changed.

Lipids are a relatively stable organic compound. It is difficult to be decomposed by bacteria. Lipids can be changed by acid compounds that produce fatty acids and glycerin. In bases state, glycerin that is released by fatty acids forms base salts.

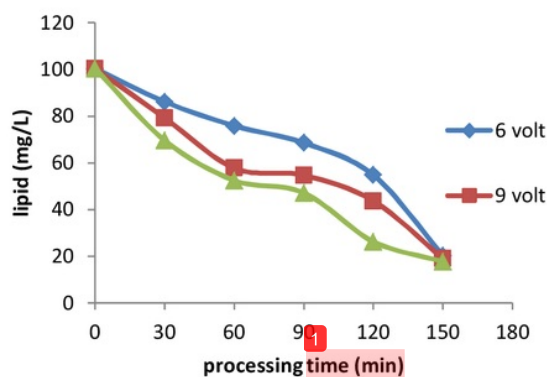


Figure 6 Effect of voltage on process time for lipids.

3.6 ¹ Effect of Voltage on Process Time for NH₃-N

Figure 7 shows that the greatest NH₃-N reduction in the POME samples was achieved with 150 minutes process time at 12 V. Under these conditions, the levels of NH₃-N in the filtrate was 0.65 mg/L, having changed from its initial

value of 3.73 mg/L. The voltage is proportional to the current: if the voltage is greater, the current flow also increases. Because current is the flow of electrons, when the current is greater, the number of electrons flowing in the EC reactor also increases. The increasing number of electrons increases the number of OH^- and H_2 gas bubbles. OH^- reacts with $\text{NH}_3\text{-N}$ at the anode. This ammonia oxidation reaction produces water and nitrogen. The more OH^- is generated by electrons, the better its performance in changing $\text{NH}_3\text{-N}$. Because the increased OH^- produced by the increased current is proportional to the voltage, the content of $\text{NH}_3\text{-N}$ in the effluent decreases.

The decrease of $\text{NH}_3\text{-N}$ in the EC process of POMEs is very important. This is because of the ammonia ($\text{NH}_3\text{-N}$), also called ammonia nitrogen, that is produced by the decomposition of organic substances of bacteria. Ammonia released in the environment forms an equilibrium reaction with ammonium ions (NH_4^+). Ammonium that experiences nitrification forms nitrite and nitrate. Dissociated ammonia are more dangerous to aquatic biota than ammonium. The ammonia value has a relation with the pH value of the water. The higher the pH of the water, the greater the dissociated ammonia content. High ammonia levels are an indication of contamination by organic materials that come from domestic waste, industrial, and agricultural fertilizer runoff [17].

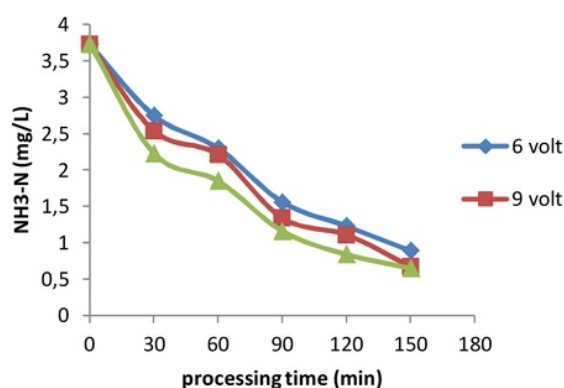


Figure 7 Effect of voltage on process time for $\text{NH}_3\text{-N}$.

3.7 Effectiveness of EC Method in POME Treatment

The effectiveness of the EC method in the POME treatment process by observing the reduction of COD, BOD_5 , TSS, lipid, and $\text{NH}_3\text{-N}$ levels and pH

values in the experiment varied. The best decrease of pollutants was found at a voltage of 12 V with a process time of 150 minutes. In this condition, the pollutants contained in the effluent dropped to below the standard set by the government.

At a voltage of 12 V, there was a greater increase of pH along with a longer process time. Effectiveness of COD removal was 82.22%, from its initial sample value of 45000 mg/L to 8000 mg/L. Effectiveness of BOD₅ removal was 80.35%, from its initial sample value of 23700 mg/L to 12000 mg/L, and effectiveness of TSS removal was 97.3%, from its initial sample value of 12000 mg/L to 324 mg/L. Effectiveness of lipid removal was 82.27%, from its initial sample value of 100.4 mg/L to 17.8 mg/L, and effectiveness of NH₃-N removal was 82.57%, from its initial sample value of 3.73 mg/L to 0.65 mg/L.

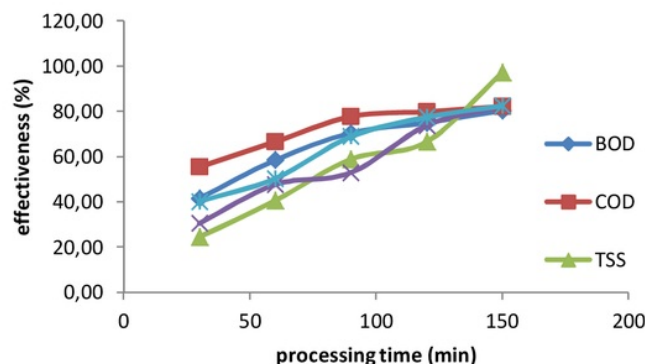


Figure 8 Effectiveness of electrocoagulation process to time at 12 V.

4 Conclusion

The optimum conditions for EC in treating POMEs with reduction parameters COD, BOD₅, TSS, lipids, and NH₃-N and an increase of pH in this study occurred at a voltage of 12 V with a process time of 150 minutes. The optimum conditions of 12 V and a process time of 150 minutes produced the greatest effectiveness of the EC method in POME treatment. The effectiveness of removal for COD was 82.22%, for BOD₅ 80.35%, for TSS 97.3%, for lipids 82.27%, and for NH₃-N 82.57%. The greater the voltage, the greater the current flow. The greater the current flow and the longer the process time, the higher the desired chemical reaction. The resulted dissolution of the aluminum electrodes during the electrocoagulation process was 2.194 gr.

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